L. H. Ulich

The Reactions between Acid Halides and Aldehydes

THE REACTIONS BETWEEN ACID HALIDES AND ALDEHYDES

BY

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Lynne Herman Ulich

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BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF Doctor of Philosophy

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L. H. Ulich.

I. INTRODUCTION

Since the reaction between acid halides and aldehydes had not been thoroughly investigated, a systematic study was begun, in this laboratory, of the addition compounds formed by the action of aliphatic and aromatic acid halides upon aliphatic and aromatic aldehydes, to determine the scope, the nature of the products formed, and their reactions. One paper[1] has already been published, giving a description of a series of addition compounds prepared by the action of benzaldehyde and certain substituted benzaldehydes on different aromatic acid chlorides and bromides and a description of a series of addition compounds of oxalyl bromide and aromatic aldehydes. A proof of the structure of these compounds in the aromatic series was given, together with a description of the reactions of the addition compounds with various reagents.

A second paper[2], as yet unpublished, contains a description of a further series of addition compounds between certain aromatic aldehydes and various substituted and unsubstituted aromatic acid halides. An extensive study of the reactions of the benzaldehyde-benzoyl bromide addition compound upon various rea ents such as primary, secondary and tertiary aliphatic and aromatic amines, pyridine and various metals was reported.

The present paper, the third of the series, shows by experimental data, that the addition reactions are general between aliphatic aldehydes and aliphatic acid halides and between aromatic acid halides and aliphatic aldehydes.

A description is given of a number of addition compounds, and their reactions with various reagents.

II. HISTORICAL PART

The first mention in the literature of a possible addition compound between acid halides and aldehydes, was reported by Wurtz[3]. He obtained a compound by the action of chlorine on acetaldehyde, to which the empirical formula of $C_4H_7O_2Cl$ was assigned, explaining, that in its formation acetaldehyde was first changed to its polymer $C_8H_8O_2$ and then that one H was substituted by a chlorine atom. Later Simpson[4] prepared the same compound by the action of acetyl chloride on acetaldehyde by heating the two in a sealed tube. Franchimont[5], likewise, prepared this compound and determined its physical constants more accurately using paraldehyde instead of acetaldehyde. Finally, Schiff[6] proved the structure of the compound to be $CH_3CHCl-O-COCH_3$, for by treating the addition product with potassium acetate he obtained ethylidene diacetate,

$$CH_3CH\begin{matrix} O-COCH_3 \\ O-COCH_3 \end{matrix}$$

This latter compound had been prepared previously by Geuther[7] from the action of $(CH_3CO)_2O$ on CH_3CHO, and the physical constants checked throughout. Rubencamp[8] prepared a number of similar addition compounds by the action of propionyl, butyryl and valeryl chlorides upon acetaldehyde. He also proved their structure by the formation of ethylidene derivatives with silver salts of fatty acids. A summary of his work appears in the following table.

TABLE I.

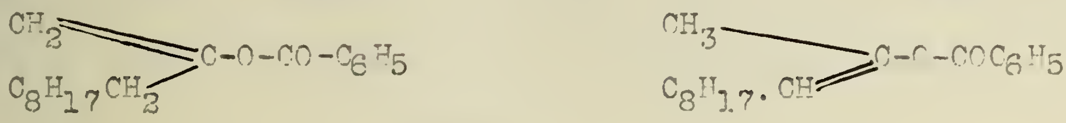
Addition Product	B.P.	Action of	Product Formed	B.P.
CH_3CHO CH_3COCl	121.5°	$AgC_2H_3O_2$	$CH_3CH\begin{matrix} O-OC_2H_3 \\ O-OC_2H_3 \end{matrix}$	168.8°
CH_3CHO CH_3CH_2COCl	135°	$AgC_3H_5O_2$	$CH_3CH\begin{matrix} O-OC_3H_5 \\ O-OC_3H_5 \end{matrix}$	192.3°
CH_3CHO $CH_3CH_2CH_2COCl$	149°	$AgC_4H_7O_2$	$CH_3CH\begin{matrix} O-OC_4H_7 \\ O-OC_4H_7 \end{matrix}$	215.5°

(Table I Continued)

Addition Product	B.P.	Action of	Product Formed	B.P.
CH_3CHO $CH_3CH_2CH_2CH_2COCl$	162°	$AgC_5H_9O_2$	$CH_3CH{<}\begin{matrix}O-OC_5H_9\\ O-OC_5H_9\end{matrix}$	225°
CH_3CHO CH_3COCl	121.5°	$AgC_3H_5O_2$	$CH_3CH{<}\begin{matrix}O-OC_2H_3\\ O-OC_3H_5\end{matrix}$	176.8°
CH_3CHO CH_3CH_2COCl	135°	$AgC_2H_3O_2$	$CH_3CH{<}\begin{matrix}O-OC_2H_3\\ O-OC_3H_5\end{matrix}$	176.8°
CH_3CHO CH_3COCl	121.5°	$AgC_4H_7O_2$	$CH_3CH{<}\begin{matrix}O-OC_2H_3\\ O-OC_4H_7\end{matrix}$	192.8°
CH_3CHO CH_3COCl	121.5°	$AgC_5H_9O_2$	$CH_3CH{<}\begin{matrix}O-OC_2H_3\\ O-OC_5H_9\end{matrix}$	194.9°

Again, Henry[9] prepared and characterized the similar addition compounds between paraformaldehyde and acetyl chloride and bromide, assigning the structures CH_3COOCH_2Cl, and CH_3COOCH_2Br to the respective compounds. The isolation of further addition compounds between higher aliphatic aldehydes and acid chlorides or bromides has not been mentioned in the literature up to the present time. However, Lees[10] isolated some unsaturated esters, by refluxing mixtures of benzoyl and valeryl chlorides on certain higher aliphatic ketones. No intermediate compounds were isolated, but he intimates that addition probably first took place, and that the halogen ester formed, by continued refluxing subsequently evolved hydrogen chloride producing the unsaturated ester. Thus methyl-n-nonyl ketone reacted with benzoyl chloride to give, what he provisionally called B-benzoxy-undecylene. The question at issue was whether the benzoyl radicle was attached to carbon or to oxygen giving a diketone or a benzoxy-olefine. However, the reactions of the oil, with alcoholic potassium hydroxide to give potassium benzoate and a similar hydrolysis with hydroxylamine with the separation of methyl n-nonyl ketoxime, proved that the benzoyl radicle was not attached to oxygen but that

the substance was a benzoxy olefine. Lees explained that the most probable course of the reaction was that first the benzoyl chloride becomes attached to the carbonyl group of the ketone, forming the intermediate compound,  , which by loss of hydrochloric acid would form either of the following compounds.



I II

He did not determine exactly in which way the halogen acid was split off. Lees also prepared the analogous compounds from benzoyl chloride and methyl-n-butyl, methyl-sec. hexyl, methyl-n-heptyl ketones, and the condensation products between benzoyl chloride and acetophenone, camphor and heptaldehyde.

Descude[11] studied the action of anhydrous zinc chloride as a catalyst on certain reactions and he observed that the reaction between various aldehydes and acid chlorides, which previously had been found necessary to heat in a sealed tube to isolate the addition compound, ran smoothly at room temperature and ordinary pressure in the presence of anhydrous zinc chloride. Descude was not able to isolate any definite addition compounds between aliphatic ketones and acetyl and benzoyl chlorides, in the presence of anhydrous zinc chloride.

In this way acetone and acetyl chloride with zinc chloride, gave mesityl oxide and phorone, while acetone and benzoyl chloride reacted in an analogous manner. The mechanism of the reaction, he presumes is as follows:

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{=}O + CH_3{-}CO{-}CH_3 + CH_3COCl \longrightarrow CH_3COOH + \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CCl{-}CH_2COCH_3$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CCl{-}CH_2\,COCH_3 \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{-}CH{-}COCH_3 + HCl$$

In a similar manner in the aromatic series, zinc chloride catalyzes the reaction between benzoyl chloride and para formaldehyde in the cold. Descude found that under the same conditions benzoyl chloride reacted with paraldehyde and benzaldehyde with acetyl and benzoyl chlorides but could not isolate definite addition compounds. He also prepared a number of different homologues of chlor methyl benzoate, a list of which appear in the following table.

TABLE II.

Addition Compound	B.P.	
chlor methyl propionate	128-130°	ordinary pressure
chlor methyl iso-butyrate	130-140°	ordinary pressure
chlor methyl n-butyrate	150°	745 mm. pressure
chlor methyl iso-valerate	170-172°	ordinary pressure
chlor methyl benzoate	116°	10 mm. pressure
chlor methyl o-toluate	125-126°	15 mm. pressure
chlor methyl m-toluate	130-132°	20 mm. pressure
chlor methyl p-toluate	136°	20 mm. pressure
chlor methyl phenyl acetate	Boiling point not given	

Paal[12], by the action of zinc dust on certain aldehydes and ketones with acid halides obtained products, which indicated that addition compounds had first formed although these intermediate products were not isolated. Thus, benzaldehyde and acetyl chloride in the presence of zinc dust gave hydrobenzoin-diacetate as follows:

$$\begin{matrix} C_6H_5CHO \\ C_6H_5CHO \end{matrix} + \begin{matrix} CH_3COCl \\ CH_3COCl \end{matrix} + Zn \longrightarrow ZnCl_2 + \begin{matrix} C_6H_5-CHOCOCH_3 \\ C_6H_5CHOCOCH_3 \end{matrix}$$

Similarly benzo-phenone gave sym-tetraphenyl ethylene glycol diacetate, which broke down to α-benz pinakolin and acetic anhydride, as

$$\begin{matrix}(C_6H_5)_2{=}C{=}O \\ (C_6H_5)_2{=}C{=}O\end{matrix} + \begin{matrix}CH_3COCl \\ CH_3COCl\end{matrix} + Zn \longrightarrow ZnCl_2 + \begin{matrix}(C_6H_5)_2{=}C\text{-}OCOCH_3 \\ | \\ (C_6H_5)_2{=}C\text{-}OCOCH_3\end{matrix}$$

$$\begin{matrix}(C_6H_5)_2{=}C\text{-}O\text{-}OCOCH_3 \\ | \\ (C_6H_5)_2{=}C\text{-}O\text{-}OCOCH_3\end{matrix} \longrightarrow \begin{matrix}(C_6H_5)_2{:}C \\ | \\ (C_6H_5)_2{:}C\end{matrix}\!\!>\!O + (CH_3CO)_2O.$$

In the aromatic series, Wöhler and Liebig[13] obtained a solid by the action of bromine upon benzaldehyde and which they supposed to be benzoyl bromide. Later, Claisen[14] isolated the same compound by the action of benzoyl bromide upon benzaldehyde, and suggested that the substance was probably an addition compound of the formula $C_6H_5CHBrOCOC_6H_5$, although he did not definitely prove its structure. Laurent and Gerhardt[15] obtained the analogous chlorine compound by the similar action of chlorine on benzaldehyde and which Schiff[16] also obtained by the action of benzoyl chloride upon benzaldehyde. Recently Staudinger and Anthes[17] isolated the corresponding iodine compound by the action of benzoyl iodide upon benzaldehyde. It was a colorless, crystalline unstable compound, which they called iod benzyl benzoate.

Staudinger[18] studied the action of oxalyl chloride on the carbonyl group of aldehydes and ketones in replacing the oxygen by two chlorine atoms. Heat caused this reaction to go practically quantitatively. However, in two cases, namely benzaldehyde and cinnamyl aldehyde, intermediate addition products were isolated when two mols of the aldehyde and one mol of oxalyl chloride in petrol ether were allowed to stand for several days at room temperature. These addition products were somewhat unstable solids to which Staudinger assigned the following structure $\begin{matrix}R\text{-}CHCl\text{-}O\text{-}CO \\ R\text{-}CHCl\text{-}O\text{-}CO\end{matrix}$. He also mentions that benzaldehyde and oxalyl bromide reacted under similar conditions to give the analogous bromine addition compound, which

was an unstable solid. Finally, and more recently, Adams and Volwiler[1] have prepared a series of the addition products between aromatic acid halides and aldehydes. Definite addition products of varying degree of stability were isolated in pure state between benzoyl bromide, benzoyl chloride and a number of its substitution products, and oxalyl bromide with various aromatic aldehydes. The constitution of the products formed was proved to be RCHXOCOR (or RCHXOCOCOOCHXR when oxalyl halides were employed), for on treating the benzaldehyde-benzoyl bromide addition product with silver benzoate in absolute ether, benzilidene dibenzoate was obtained. This latter compound had previously been prepared by Wegscheider and Spath[19] from benzaldehyde and benzoic anhydride, and the physical constants of the two compounds agreed. The mechanism of the reaction from phenylbromomethyl benzoate and silver benzoate is as follows, $C_6H_5CHBrOCOC_6H_5 + C_6H_5COOAg \longrightarrow AgBr + C_6H_5CH(OCOC_6H_5)_2$ French[2] has further prepared a series of aldehyde acid halide addition products in the aromatic series, and has studied thoroughly their reactions as typified by phenyl bromomethyl benzoate. He has shown that (1) primary and secondary aliphatic amines react with phenybromomethyl benzoate to give substituted benz amides, be nzaldehyde and the hydrobromide of the amine. (2) Tertiary aliphatic amines and pyridine react to form additive compounds. (3) Primary aromatic amines react to produce the hydrobromides of benzylidene anilines. (4) Secondary and tertiary aromatic amines react to yield dyes of the triphenyl methane series. (5) Metals react to give dibenzoates of sym. diphenyl glycols, and (6) aluminum amalgam, potassium cyanide, potassium acetate, potassium benzoate and potassium hydroxide completely hydrolyze the compound.

Thus, the reactions of phenyl bromo methyl benzoate are those which might be expected from a mere mixture of benzaldehyde and benzoyl bromide, while others, especially with aniline, tertiary aliphatic amines, pyridine, and silver salts of organic acids are characteristic of the addition compound.

III THEORETICAL PART.

The preparation of addition compounds between acid halides and aldehydes in the aliphatic and aromatic series involves widely different methods. In the aromatic series, the addition products as a rule are solids and are produced by merely mixing the aldehyde and acid halide in equimolecular proportions in a tightly stoppered flask and allowing to stand at room temperature until solidification has taken place. In the aliphatic series, the addition compounds thus far produced are all liquids, which must be purified by fractional distillation under ordinary or diminished pressure and it was found necessary to heat the acid halide and aldehyde in a sealed flask at 100-130° in order to produce the substances. Descude[11], however, found that zinc chloride catalyzed the reaction between acid halides and aldehydes at room temperature and without exception the addition compounds between higher aliphatic aldehydes and acid chlorides mentioned in this paper have been prepared either at room temperature or heating on the water bath at 90° under ordinary pressure, and in the presence of anhydrous zinc chloride. However, it was in the aromatic-aliphatic series that the most striking difference in the method of preparation of the addition compounds was observed. Benzoyl chloride and n-butyl, iso-valeryl and heptaldehydes did not form addition compounds at room temperature even in the presence of zinc chloride. In fact, it was found necessary to reflux the mixture for a short time at its boiling temperature for the reaction to take place. And in the case of benzoyl chloride and paraformaldehyde and paraldehyde it was necessary to heat the mixture on the water bath at 90° for several hours before the addition product formed. In the formation of the addition compounds in the aromatic-aliphatic series a peculiar side reaction takes place, namely, the formation of benzoic or substituted benzoic acids, de-

pending on the nature of the aromatic acid halide used. The formation of these acids, which necessarily decreases the yield of the final addition product, might be explained by the fact that the aliphatic aldehydes employed in the reaction contained a trace of water which would hydrolyze the acid halide to the free acid. A second supposition would be that the addition compound after forming was unstable and decomposed in some manner to regenerate the free acid. Another hypothesis is that a secondary reaction takes place, which produces water and which in turn hydrolyzes the acid halide.

The first supposition is highly improbable, for the aliphatic aldehydes used were carefully dried over calcium chloride, and furthermore, the amounts of free acid formed in any one experiment were entirely too large from what might be expected by the trace of moisture still left in the reagents. Equal care was exercised to prevent the moisture in the air from entering during the reaction. The second supposition is contrary to the data obtained by experiment and the properties of this particular type of addition compound in the aromatic-aliphatic series. In the first place, no addition product was obtained at all at room temperatures, but after refluxing at higher temperatures for a short time, the addition product was obtained, an experience which does not indicate especial instability. In fact, the benzoyl chloride-aliphatic aldehyde addition products were sufficiently stable to permit shaking their ether solutions with 10% sodium carbonate (to remove the acid formed in the reaction) without decomposition. Even Lees[10] found it necessary to reflux benzoyl chloride and heptaldehyde for six hours at a high temperature before he obtained the unsaturated ester $C_6H_5COOCH{=}CH(CH_2)_4CH_3$, which he called α benzoxy α heptylene and which was probably produced by the loss of hydrogen chloride

from the halogen ester. The conclusion was therefore drawn that the formation of free acid in the experiments was due to a secondary reaction.

A probable explanation of this secondary reaction is that the particular aldehyde employed undergoes an aldol condensation, with the production of water. The water formed in turn would hydrolyze the acid chloride. That water was actually formed during the course of the reaction was observed in many of the experiments. If this secondary reaction was caused by water formed in an aldol condensation of the aldehyde, one would expect to obtain more free acid when employing an aldehyde such as n-butyl, than the amount formed when using a higher aldehyde such as heptaldehyde, for the former undergoes an aldol condensation more readily than the latter. This was actually observed in experiment. That this secondary reaction is probably due to an aldol condensation of the aliphatic aldehydes employed was also borne out by Lees, who observed the formation of large amounts of benzoic acid in the preparation of α benzoxy α heptylene and which he explained in a similar fashion.

That the free acid formed in the reactions with benzoyl chloride was due to an aldol condensation of the aliphatic aldehyde was further indicated by experiment. Acetaldehyde was obtained from its polymer paraldehyde by distillation with a small amount of concentrated sulphuric acid. Acetaldehyde will undergo an aldol condensation more readily than its higher homologues, and consequently when the free aldehyde is heated on the water bath with benzoyl chloride, there should be more benzoic acid formed if the theory is true. In the experiment performed, the addition compound was not isolated but a high boiling condensation product of acetaldehyde and all of the benzoyl chloride was converted to benzoic acid.

However, when the polymer paraldehyde was used, the amount of benzoic acid formed was small in comparison, which indicates that as the free aldehyde is liberated, the reaction to form the halogenated ester is more rapid than the aldol condensation, the benzoyl chloride always being in excess.

Again, when benzoyl chloride was refluxed 13 hours with chloral, although an addition compound was not isolated, yet there was no benzoic acid formed in the reaction. It will be observed that in **chloral** CCl_3CHO, all of the hydrogen atoms on the alpha carbon atom are substituted with chlorine atoms and therefore is incapable of undergoing an aldol condensation. Therefore, since there was no benzoic acid formed in this case, the conclusion was drawn that the acid formed in the other experiments came from hydrolysis of the acid halide by the water eliminated during an aldol condensation of the unsubstituted aliphatic aldehydes used.

In the aromatic series, the ease of formation and the stability of the addition compounds was greatly influenced by the nature of the substituent groups in the ring of both the acid halide and aldehyde. Thus, the indications were that negatively substituted acid halides or aldehydes enter into the addition reactions less easily than the unsubstituted ones. In the aliphatic series, no such generalization could be drawn, in as much as most of the aliphatic aldehydes and acid halides employed were unsubstituted ones. However, it was found that the nature of the simple aliphatic halide used did influence the ease of reaction and stability of the compound formed. Thus, acid bromides reacted with greater violence and the addition compounds produced were more unstable than the corresponding acid chloride compounds. This characteristic is probably due to the fact that hydrogen bromide as a rule is

more easily split off from compounds than hydrogen chloride.

The addition reactions between the aldehydes and acid halides studied was greatly influenced by the size of the molecule of the aldehyde and to a less extent, the acid halide. Acetyl chloride reacted more violently and greater speed with acetaldehyde than heptaldehyde. It was necessary to heat acetyl chloride and heptaldehyde on the water bath for some time to obtain the halogenated ester whereas acetyl chloride and acetaldehyde react immediately at room temperature. Valeryl chloride reacted vigorously with paraldehyde and with more violence than iso-valeryl aldehyde with acetyl chloride. The conclusion was, therefore, drawn that the number of carbon atoms in the aldehyde used influenced the reactions to a marked degree, the lower members having a greater speed of reaction. The difference in reactivity of the various acid halides, other than acetyl chloride, with any particular aldehyde was not marked, but in this case also the nature of the aldehyde was most important.

In general, the stability of the aliphatic acid halide-aldehyde addition products prepared was decreased, the higher one advanced in the homologous series and all were easily decomposed by water in a short time.

The aromatic acid halide-aliphatic aldehyde addition compounds, on the contrary, although formed with greater difficulty when once produced were stable for an indefinite period in water and even more so than benzoyl chloride itself.

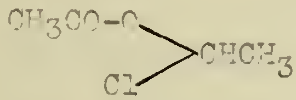
The constitution of the aldehyde-acid chloride addition products in the aliphatic series has already been proved by Schiff[6] with the acetaldehyde-acetyl chloride addition compound. Wurtz[3] who first prepared this substance proposed either one of the two

following formulae:

I

II

Both of these formulae show an addition of one molecule of acetaldehyde with one of acetyl chloride but each one in turn involves linkage of the two molecules through oxygen, a linkage which would in all probability be very unstable. This is not particularly true for chlor ethyl acetate is a comparatively stable liquid. However, Schiff definitely disproved both of these formulae, and established the fact that the addition product between acetaldehyde and acetyl chloride was a halogen ester and assigned to it the following formula:



III

This structure of the compound was derived from the fact that on treating the purified addition compound dissolved in absolute alcohol with potassium acetate, double decomposition took place to form ethylidene diacetate. The mechanism of the reaction, therefore, was as follows:

$$CH_3COOCHClCH_3 + CH_3COOK \longrightarrow (CH_3COO)_2{=}CHCH_3 + KCl$$

Ethylidene diacetate had previously been prepared by Geuther[7] from acetaldehyde and acetic anhydride, and the physical constants of the two compounds compared favorably. Rubencamp[8] arrived at the same conclusion by treating the compound with silver acetate in absolute ether solution, whereby ethylidene diacetate and silver chloride was obtained. He also proved that the structures of the corresponding addition compounds between acetaldehyde and propionyl,

butyryl, and valeryl chlorides was the same for on treating these compounds in a similar manner with silver propionate, butyrate and valerate respectively, ethylidene dipropionate, dibutyrate and divalerate were obtained in the order named. These reactions can best be explained by formula III, assigned to the acetaldehyde-acetyl chloride addition compound by Schiff. In as much as the structure of the addition compounds between formaldehyde, acetaldehyde and acetyl chloride, together with a few of their homologues in the aliphatic series, had already been proved, it seemed unnecessary to establish further the structure of the addition compounds of the higher aliphatic aldehydes and acid chlorides given in this paper, but to let an elementary analysis for halogen suffice.

However, in one reaction tried, namely that of potassium hydroxide on the acetyl chloride-heptaldehyde addition compound, products were obtained which indicated the probable structure of the compound. In this reaction, potassium acetate, potassium chloride and heptaldehyde were produced, which would indicate that the addition compound was a halogen ester and similar in structure to its lower homologues.

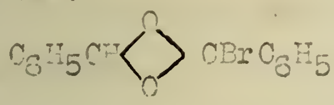
The mechanism of the formation of these products might be represented by the following equation,

$$CH_3COO\text{-}CH\,Cl\,(CH_2)_5CH_3 + 2KOH \longrightarrow CH_3COOK + KCl + H_2O + CH_3(CH_2)_5CHO.$$

It is true that a mere mixture of acetyl chloride and heptaldehyde might yield these same products with potassium hydroxide, but it is hard to conceive that if the substance was a mere mixture why the boiling point under diminished pressure was so constant. A mere mixture of an aldehyde and acid chloride, even though possibly having a constant boiling point would show some signs of reaction or decomposition after standing for some time and this par-

ticular compound remained perfectly colorless with no signs of decomposition for an indefinite period.

In the aromatic series, the structure of the aldehyde-acid halide addition compounds has been proved by Adams and Volwiler[1] using the product obtained by the action of benzoyl bromide upon benzaldehyde. In the aromatic series, again there are three formulae, which might be advanced to explain the reactions of the compounds.



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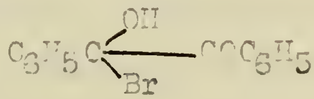
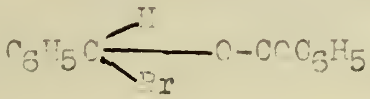


II



III

The first formula involves an ether linkage, an unstable and improbable structure. The second formula presupposes a hydroxyl group and a halogen on the same carbon atom, an extremely unstable structure so that compounds containing this grouping have not been isolated, owing to the great tendency to split off halogen acid. The third formula, which proved to be the correct one, represents the addition compound as a halogen ester, a structure which is similar to the analogous compounds in the aliphatic series. This constitution was determined by the action of silver benzoate upon phenyl bromomethyl benzoate, whereby benzylidene dibenzoate was obtained. This latter compound was similar in all respects to the benzylidene dibenzoate prepared previously by Wegscheider and Spath[19] from the action of benzoic anhydride upon benzaldehyde.

The formation of benzylidene dibenzoate from the action of silver benzoate upon phenyl bromo methyl benzoate may be repre-

sented by the following reaction:

$$C_6H_5COO-CHBrC_6H_5 + C_6H_5COOAg \longrightarrow C_6H_5CH(OCOC_6H_5)_2 + AgBr$$

That the compounds, mentioned in this paper, obtained by the action of benzoyl chloride upon certain aliphatic aldehydes are also halogen esters of benzoic acid, may also be inferred by the action of potassium hydroxide upon them. Thus, when the compound obtained by the action of benzoyl chloride on iso-valeryl aldehyde was heated on the water bath with pulverized potassium hydroxide, it was decomposed and the products obtained were potassium benzoate, potassium chloride and isovaleryl aldehyde, as follows:

$$C_6H_5COO-CHClCH_2CH(CH_3)_2 + 2KOH \longrightarrow C_6H_5COOK + KCl + H_2O + (CH_3)_2CHCH_2CHO$$

It is therefore reasonable to maintain that all the compounds obtained by the action of acid halides upon aldehydes both in the aliphatic and aromatic series are halogen esters.

In the reactions tried, using chlor methyl acetate for the aliphatic and chlor methyl benzoate for the aromatic-aliphatic series, no different reactions were observed than those obtained by other investigators, using corresponding addition compounds.

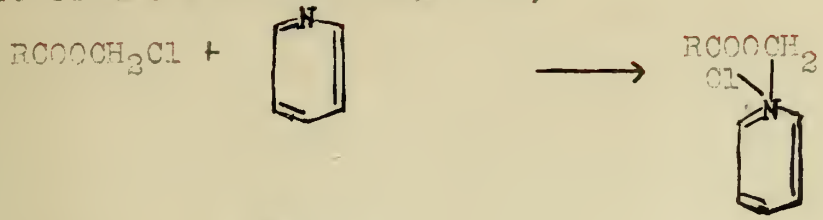
In general the reactions observed were those which might be expected from a mere mixture of the acid halide and aldehyde employed, while others were characteristic of the addition compounds. Thus, as example of the first type of reaction, ammonia, mono methyl amine, diethylamine, and aniline reacted as follows:

1. $RCOOCH_2Cl + 2NH_3 \longrightarrow RCONH_2 + NH_4Cl + CH_2O$
2. $RCOOCH_2Cl + 2CH_3NH_2 \longrightarrow RCONHCH_3 + CH_3NH_2.HCl + CH_2O$.
3. $RCOOCH_2Cl + 2(C_2H_5)_2NH \longrightarrow RCON(C_2H_5)_2 + (C_2H_5)_2NH.HCl + CH_2O$
4. $RCOOCH_2Cl + 2C_6H_5NH_2 \longrightarrow RCONHC_6H_5 + C_6H_5NH_2HCl + CH_2O$

where R represents either a methyl or a phenyl group.

Pyridine and quinoline reacted to give stable salts char-

acteristic of the addition compounds,



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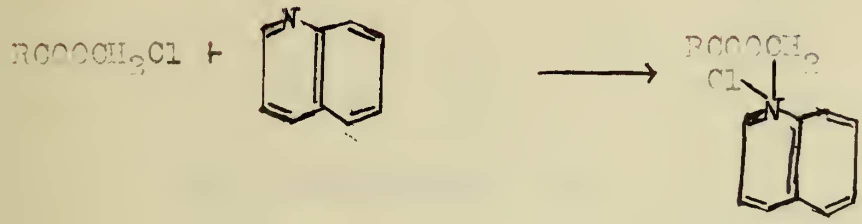

IV. EXPERIMENTAL PART

The preparation of addition compounds between aliphatic aldehydes and acid halides, and aliphatic aldehydes and aromatic acid halides involves using different methods than those employed for the preparation of the condensation products between aromatic acid halides and aromatic aldehydes. In the latter case equimolecular[1] amounts of the aromatic aldehyde and acid halide are mixed and allowed to stand at room temperature in a tightly stoppered flask until solidification occurs. In the aliphatic-aliphatic series, and aromatic-aliphatic series, the condensation products prepared are all liquids.

For the preparation of the aliphatic-aliphatic addition products the following directions are used. Equimolecular amounts of the aliphatic aldehyde and aliphatic acid halide are weighed out in a round bottom flask, which is ground to fit a water condenser. A minute quantity of anhydrous zinc chloride may be added as a catalyzer[11]. Upon mixing the aliphatic aldehyde and aliphatic acid halide, there is considerable heat evolved in many cases causing the reaction mixture to boil gently. However, the reaction soon subsides and further heating on the water bath at 90° for 3 - 4 hours is advisable. At the end of this time, the reaction mixture is distilled once under diminished pressure, the purpose of which is to prevent decomposition when zinc chloride has been used to catalyze the reaction. The reaction does not go to completion in the aliphatic series and hence the reaction products must be separated from unchanged material by efficient fractional distillations, either under ordinary or diminished pressure. In this manner, from 50-70% yield of the halogenated esters, boiling over a 2 - 3 degree range, is obtained.

It has been found that the addition products between aromatic acid chlorides and aliphatic aldehydes, with the exception of paraformaldehyde, form with more difficulty, and it is necessary even to reflux the reaction mixture for several hours. In general the method of preparation for the aromatic acid halide-aliphatic aldehyde condensation products is as follows. The aromatic acid halide is heated with a free flame and then equimolecular amounts of the aliphatic aldehyde added slowly from a dropping funnel, refluxing gently from 1 - 2 hours. The reaction mixture is allowed to cool and treated with 10% Na_2CO_3 solution and ether to remove the aromatic acid which is formed as a side reaction. It has been found that the aromatic acid halide-aliphatic aldehyde condensation products are stable toward water and in ether solution stable to 10% Na_2CO_3. The ether layer is separated, dried with $CaCl_2$ and distilled, the ether under ordinary pressure and the residual oil under diminished pressure. The yields of the condensation products in this series are from 40-50%, based on the amount of aldehyde used. The smaller yields are probably due to the fact that a considerable portion of the aromatic acid halide is hydrolyzed by water which is formed in a secondary reaction.

In the preparation of the condensation products between aromatic acid halides and paraformaldehyde, the two are simply weighed out in a round bottom flask ground to fit a water condenser, and heated on the water bath till the solid paraformaldehyde which has been dried in an oven at 95-100° has disappeared. The reaction mixture is then distilled and fractionated directly under diminished pressure. In every case, there is a small amount of low boiling product and also high boiling, which is separated by distillation.

The formaldehyde condenses in the receivers toward the end of the distillation and at times during the distillation, probably due to the fact that there is some slight decomposition of the condensation product. The physical constants reported in this paper are in every case uncorrected.

A. Reactions of Aliphatic Aldehydes and Aliphatic Acid Halides.

1. Addition Products with Paraformaldehyde.

Paraformaldehyde and Acetyl Chloride= $CH_3C(=O)-OCH_2Cl$, chloromethyl acetate.

The paraformaldehyde used in the experiments was the ordinary commercial powder, which was carefully dried in an oven at 95-100°. The acetyl chloride used was freshly redistilled to insure a pure product. The $ZnCl_2$ was fused and powdered before each experiment. 30 grams (1 mol) of paraformaldehyde was added to 78 grams (1 mol) acetyl chloride in a r.b. flask. There was no appreciable reaction in the cold. On adding a pinch of fused, powdered zinc chloride[11], a reaction took place at once with an evolution of heat. The flask was attached to a water condenser and heated on the water bath at 90° until the paraformaldehyde had disappeared (2 hours). The reaction mixture was then transferred to a Claisen bulb and distilled under diminished pressure (to prevent decomposition from the zinc chloride). Most of the liquid boiled between 65-75° at 70 mm. pressure. The product was separated into 3 fractions by distillation under ordinary pressure.

I. Fraction B.P. 100-110° 748 mm.

II. Fraction B.P. 110-130° 748 mm.

III. Fraction B.P. 130-170° 748 mm.

After several fractional distillations, a product was obtained which boiled constant on redistillation, at 113-115° 748 mm. and weighed 35 grs. The yield was 53%.

The low boiling portion, about 15 gm., consists largely of dichloro dimethyl ether, and the high fraction, about 17 gms. of methylene diacetate formed according to Descude[11] by the following reaction.

$2\ CH_3COOCH_2Cl \longrightarrow (CH_3{-}CO)_2O + O(CH_2Cl)_2.$ B.P. 105°

$(CH_3{-}CO)_2O + CH_2O \longrightarrow (CH_3.COO)_2CH_2.$

The boiling point of chloro methyl acetate given in the literature is 115° at 758 mm[11]. The product was a colorless liquid with penetrating odor and did not decompose on standing in a tightly stoppered reagent bottle.

Subst., 0.2032; AgCl, 0.2820.

Calc. for $C_3H_5O_2Cl$: Cl, 32.7%. Found: 32.95%.

Paraformaldehyde and Propionyl Chloride= $CH_3CH_2COO{-}CH_2Cl$,
Chloro Methyl Acetate

The propionyl chloride was prepared by the action of oxalyl chloride (3 mols) upon propionic acid[30] (2 mols) and redistilled twice for purification, B.P. 80-81° at 750 mm. 15 grams of dry paraformaldehyde was added to 46 grams of propionyl chloride. There was a slight reaction upon mixing the two, however after adding a pinch of fused zinc chloride, the reaction became vigorous, with evolution of considerable heat. The mixture was heated on the water bath until the paraformaldehyde had disappeared (30 minutes) and then transferred to a Claisen bulb and distilled under diminished pressure. Most of the liquid boiled between 68-80° at 40 mm. The distillate was separated into three portions by fractional distillation under ordinary pressure using a good column.

I. Fraction B.P. 100-125° at 740 mm.

II. Fraction B.P. 125-135° at 740 mm.

III. Fraction B.P. 135-165° at 740 mm.

After several fractional distillations 30 grams of a product was obtained which proved to be chloro-methyl propionate and boiled at 128-130° at 740 mm. The literature[11] gives the boiling point as 128-130°, no corresponding pressure being recorded. Fractions I (10 grs.) and III (10 grs.) probably consist of dichlordimethyl ether and the dipropionate of methylene as indicated above. The halogenated ester was a colorless liquid, with a sharp odor. The yield was 50%.

Paraformaldehyde and Butyryl Chloride= $CH_3CH_2CH_2CO-O-CH_2Cl$, Chloro Methyl Butyrate.

The butyryl chloride used in the reaction was prepared by the action of thionyl chloride (3 mols) on butyric acid (2 mols). The product used boiled at 99-100° at 740 mm. 53 grams of the acid chloride was weighed out in a r.b. flask, together with 15 grams of dry paraformaldehyde. There was no evidence of a reaction in the cold. After adding a pinch of fused zinc chloride, a vigorous reaction ensued, the reaction was completed by heating upon the water bath at 90° till the paraformaldehyde had disappeared (1 hr.). The mixture was then transferred to a Claisen flask and distilled under diminished pressure, the greater portion boiling at 70-100° at 40 mm. The product was then separated into three fractions by distillation under ordinary pressure.

I. Fraction B.P. 120-140°.

II. Fraction B.P. 140-150°.

III. Fraction B.P. 150-170°.

The three portions were refractionated several times, until a product was obtained boiling at 148-9° at 738 mm. and was chloro methyl butyrate. The literature[1] gives the boiling point as 150°[11] at 745 mm. 35 grs. of the halogenated ester was obtained, making a

yield of 51%. 20 grams of the low boiling and 15 grams of the high boiling fractions were also obtained. The addition product was a colorless liquid, with a penetrating odor. The product did not decompose on standing in a tightly stoppered reagent bottle.

Paraformaldehyde and n-Valeryl Chloride=$CH_3CH_2CH_2CH_2CO-O-CH_2Cl$, Chloro Methyl n-Valerate.

The valeryl chloride was prepared by the action of thionyl chloride (3 mols) on n-valeric acid (3 mols). 65 grs. of the acid chloride, B.P. 106-7° at 750 mm., and 15 grams of dry paraformaldehyde with a small portion of fused zinc chloride were placed in a round bottom flask. The mixture was heated on the water bath at 90° until the paraformaldehyde had disappeared (1 hour). The yellow liquid was then transferred to a Claisen bulb and distilled under diminished pressure, the greater portion boiling at 60° to 75° under 20 mm. pressure. The distillate was then separated into three fractions by distillation under ordinary pressure.

I. Fraction B.P. 120-160° at 750 mm.

II. Fraction B.P. 160-170° at 750 mm.

III. Fraction B.P. 170-200° at 750 mm.

The distillates were then refractionated several times until a product was obtained which boiled constant at 163-166° at 750 mm.

50 grams of the halogenated ester was obtained while 30 grams of the low boiling and 7 grs. of the high boiling fractions were recovered respectively. The yield was 65%, based on the products recovered. The chloromethyl n-valerate was a colorless liquid possessing a sharp odor and not decomposing on standing in a reagent bottle.

Subst., 0.1744; AgCl, 0.1550.

Calc. for $C_6H_{11}O_2Cl$: Cl, 23.6. Found, 23.9.

Paraformaldehyde and Acetyl Bromide= $CH_3CO-O-CH_2Br$, Bromo-methyl Acetate.

The acetyl bromide was prepared by the action of red phosphorus and bromine (1 mol) upon glacial acetic acid (1 mol)[21]. The product boiling at 80-81° at 750 mm. was used. 122 grs. of the acid bromide and 30 grams of dry paraformaldehyde were placed in a r.b. flask. No zinc chloride was used, as the reaction takes place with extreme violence, on merely mixing the two chemicals. It was not necessary to heat on the water bath, because the paraformaldehyde had all disappeared within 10 minutes, its own heat of reaction being sufficient to carry the reaction to completion. The brown liquid was then transferred to a Claisen bulb and distilled under diminished pressure, the main portion boiling at 50-80° at 18 mm. The distillate was separated into three fractions by distillation under ordinary pressure.

I. Fraction 80-128° at 750 mm.

II. Fraction 128-138° at 750 mm.

III. Fraction 138-170° at 750 mm.

After repeated fractionations, a product was obtained which boiled constant at 130-133° at 750 mm. The literature[2] gives the boiling point of the brominated ester[22] as 130° at 746 mm. 80 grams of the addition product was obtained while the low boiling fraction was composed of 30 grams and the high boiling fraction 30 grams of the distillate. The yield was 60%, based on the products recovered. Bromo-methyl acetate is a colorless, heavy liquid, fuming slightly in the air, and is stable.

Paraformaldehyde and Chloro Acetyl Chloride= $CH_2ClCO-OCH_2Cl$, Chloro Methyl Mono Chloro Acetate.

In order to show that the reaction between paraformalde-

hyde and aliphatic acid halides was general, a substituted acid chloride was used. The acid chloride employed was mono-chloro acetyl chloride, prepared by the action of oxalyl chloride (2 mols) on mono chloroacetic acid[20] (1 mol). The product used in the reaction boiled at 103-106° at 750 mm. 56 grams of the acid chloride and 15 grams of dry paraformaldehyde, with a pinch of fused zinc chloride were placed in a r.b. flask. The reaction mixture was heated on the water bath at 90° for 4 hours until the paraformaldehyde had disappeared. The liquid was distilled under diminished pressure, the greater portion boiling at 45-110° at 40 mm. The mixture was then separated into 3 portions by fractional distillation under ordinary pressure.

I. Fraction B.P. 95-105° at 745 mm.

II. Fraction B.P. 125-135° at 745 mm.

III. Fraction B.P. 140-200° at 745 mm.

After several fractional distillations, a product was obtained which boiled constant at 130-2° at 745 mm. and weighed 30 grams. The low boiling fraction, about 15 grams, was probably unchanged acid halide and the high boiling fraction, consisting of 8 grams, was probably a high boiling condensation product. The yield was 50%. The halogenated ester was a heavy, colorless liquid, with a sharp odor and was stable.

Subst., 0.1477; AgCl, 0.2892.

Calc. for $C_3H_4O_2Cl_2$; Cl, 48.8. Found, Cl, 48.5.

2. Addition Products with Paraldehyde.

Paraldehyde and Acetyl Chloride= $CH_3COO-CHClCH_3$, α chloro-ethyl acetate.

Acet-aldehyde itself was not used in the experiments since it was found by Simpson[4] and Franchmont[5] that its polymer paralde-

hyde would condense equally as well. 117 grs. (1 mol) of freshly distilled acetyl chloride and 66 grams of paraldehyde were placed in a round bottom flask ground to fit a water condenser. A marked reaction took place on mixing the two chemicals, accompanied by an evolution of heat. The reaction mixture was then heated on the water bath for 3 hours, after which it was transferred to a Claisen bulb and distilled under diminished pressure. The product boiled at 50-70° at 30 mm. The distillate was then separated into 3 portions by fractional distillation.

I. Fraction B.P. 60-110° at 740 mm.

II. Fraction B.P. 110-130° at 740 mm.

III. Fraction B.P. 130-158° at 740 mm.

After several fractionations 95 grams of a product was obtained, B.P. 113-116° at 740 mm. The literature[5] gives the boiling point of chloro ethyl acetate as 121.5° at 746 mm. Several different runs were made but in no case did the larger portion of the liquid boil at this temperature. 30 grams of the low boiling and 38 grams of the high boiling fraction was also obtained. The yield of the α chlor ethyl acetate was 62%. The addition product was a colorless, heavy liquid, with a characteristic ester odor and which turned slightly yellow on standing.

Subst., 0.1865; AgCl, 0.2300.

Calc. for $C_4H_7O_2Cl$: Cl, 33.97. Found, 32.3

Paraldehyde and Propionyl Chloride= $CH_3CH_2CO\text{-}O\text{-}CHClCH_3$,
α chloro ethyl propionate.

49 grams of propionyl chloride, prepared by the method cited above, and 22 grams of paraldehyde were placed in a round bottom flask and heated on the water bath at 90° for one hour. The liquid, which had turned dark, was distilled under diminished pres-

sure. The greater portion of the reaction mixture boiled at 65-75° at 70 mm. The liquid was then separated by fractional distillation into three portions.

I. Fraction B.P. 100-130° 740 mm.

II. Fraction B.P. 130-140° 740 mm.

III. Fraction B.P. 140-180° 740 mm.

On refractionating several times, 30 grams of a product was obtained with constant boiling point of 133-5° at 740 mm. The literature[8] gives the boiling point of the halogenated ester as 134-136°, no pressure being given. 15 grams of the low boiling fraction and 10 grams of the high boiling fraction were also obtained. The yield of the addition product was 55%. The halogenated ester was a heavy, colorless liquid when freshly distilled, but turned dark on standing, there being some decomposition. It possessed the characteristic odor of all the halogenated esters.

Subst., 0.1940. AgCl, 0.2068.

Calc. for $C_5H_9O_2Cl$: Cl, 26.00. Found, 26.3.

Paraldehyde and Butyryl Chloride= $CH_3CH_2CH_2COO-CHClCH_3$,
α chloro ethyl butyrate.

53 grams of butyryl chloride, prepared as indicated above, and 22 grams of paraldehyde were placed in a round bottom flask and heated on the water bath at 90° for 1 hour. The liquid, which had turned dark during the reaction, was transferred to a Claisen flask and distilled under diminished pressure, the main portion boiling at 75-85° at 50 mm. The product was then separated by fractional distillation.

I. Fraction B.P. 130-145° 740 mm.

II. Fraction B.P. 145-155° 740 mm.

III. Fraction B.P. 155-190° 740 mm.

Repeated fractionation gave 35 grams of a constant boiling product, 150-153° at 740 mm. The literature[8] gives the boiling point of the halogenated ester as 149-151°, no pressure being given. The low boiling fraction consisted of 20 grams, and the high boiling fraction 10 grams. The yield of α chloro ethyl butyrate was 50%. The halogenated ester was a heavy, colorless liquid, decomposing somewhat on standing. It had a sharp odor.

Subst., 0.1972, AgCl, 0.1904.

Calc. for $C_6H_{11}O_2Cl$: Cl, 23.81. Found, 23.59%.

Paraldehyde and Valeryl Chloride= $CH_3(CH_2)_3COOCHClCH_3$, α chloro-ethyl valerate.

75 grams of valeryl chloride, prepared by the method already indicated, and 27 grams of paraldehyde were placed in a round bottom flask and heated on the water bath at 90° for 2 hours. At the end of that time, the dark liquid was distilled under diminished pressure, the main product boiling at 95-100° at 12 mm. The distillate was then separated by fractional distillation under ordinary pressure.

I. Fraction B.P. 100-159° at 750 mm.

II. Fraction B.P. 159-169° at 750 mm.

III. Fraction B.P. 169-200° at 750 mm.

After several fractionations, 60 grams of a product boiling constant at 163-165° at 750 mm. was obtained. The literature[8] gives the boiling point of the halogen ester as 162-164°, no pressure being given. The low boiling fraction composed 30 grams and the high boiling fraction 15 grams of the distillate. The yield of the addition product was 63%. The halogenated ester was a heavy, colorless liquid, which decomposed slowly on standing.

Subst., 0.2270; AgCl, 0.1944.

Calc. for $C_7H_{13}O_2Cl$: Cl, 21.55. Found, 21.2.

Paraldehyde and Acetyl Bromide= $CH_3CO-O-CHBrCH_3$,
α Bromo Ethyl Acetate.

123 grams of acetyl bromide, prepared by the method cited above, and 44 grams of paraldehyde were weighed out in a round bottom flask. The two reacted almost instantly, with evolution of much heat. The reaction was finished by heating on the water bath at 90° for 3 hours, and then distilled under diminished pressure. The main portion of the dark liquid boiled at 70-80° at 30 mm. The distillate was then separated by fractional distillation under ordinary pressure.

I.	Fraction	B.P. 110-120°	738 mm.
II.	Fraction	B.P. 120-128°	738 mm.
III.	Fraction	B.P. 128-140°	738 mm.

Repeated fractionations gave 92 grams of a product boiling constant at 123-125° at 738 mm. There was 30 grams of the low boiling fraction and 18 grams of the high boiling fraction. The brominated ester was a heavy, colorless, fuming liquid which decomposed easily. The yield of addition product was 65%.

Subst. 0.2344; AgBr, 0.2644

Calc. for $C_4H_7O_2Br$: Br, 47.8%, Found, 48.1%.

Paraldehyde and Bromo Acetyl Bromide= $CH_2BrCOO-CHBrCH_3$,
α Bromo ethyl mono bromo acetate.

The reaction between paraldehyde and the substituted aliphatic acid halide, brom acetyl bromide was studied, to show that the condensation reactions between paraldehyde and aliphatic acid halides was also of general application. The bromo acetyl bromide was prepared by the method of Hell[33], Volhard[34], Zelinsky[35], and the product used boiled at 148-150° at 750 mm. 75 grams of the acid halides and 11 grams of paraldehyde were placed in a round bottom flask ground to fit a water condenser. There was a vigorous

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[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

reaction upon mixing the two chemicals, which was completed by heating on the water bath at 90° for 1 hour. The liquid, which had turned a deep red color, during the reaction from liberation of free bromide, was transferred to a distilling flask, as described by Noyes[26], without the separatory funnel attached, and distilled under diminished pressure. The product was distilled under diminished pressure, because there was decided decomposition of the liquid at high temperature and ordinary pressure.

After repeated fractionations in vacuum, the reaction mixture was separated as follows:

I. Fraction B.P. 45- 90° at 18 mm. 10 grams.

II. Fraction B.P. 90-100° at 18 mm. 35 grams.

III. Fraction B.P. 130-140° at 18 mm. 12 grams.

The low boiling fraction was largely unreacted acid halide and the high boiling fraction complex condensation products. The middle fraction, however, contained a constant boiling product, 95-97°, at 8 mm. which was α bromo ethyl mono brom acetate. It was a heavy colorless liquid, with sharp odor, which decomposed easily on standing. The yield was 60%.

Subst. 0.2060; AgBr, 0.3175.

Calc. for $C_4H_6O_2Br$: Br, 65.05. Found, 65.3.

3. Addition Products with Isobutyl Aldehyde.

Isobutyl Aldehyde and Acetyl Chloride=$CH_3CO\text{-}O\text{-}CHClCH\langle^{CH_3}_{CH_3}$,

α chloro iso-butyl acetate.

The iso-butyl aldehyde was prepared by the method described in Vanino[27] from iso-butyl alcohol. The product boiling at 67-69° was used. The acetyl chloride was redistilled. 50 grams of the aldehyde and 54 grams of acetyl chloride were placed in a

round bottom flask. The reaction mixture warmed immediately, and was finished by heating on the water bath at 90° for 1 hour. The liquid which had turned dark during the reaction was then distilled under diminished pressure, the product boiling at 40-105° at 50 mm. The addition products with aliphatic acid halides and aliphatic aldehydes other than paraformaldehyde and paraldehyde were fractionated under vacuum, to prevent the decomposition which seemed to take place at higher temperatures and ordinary pressure, and therefore, the physical constants of the former are given under diminished pressure only. After repeated fractionations in vacuum, the following fractions were obtained.

I. Fraction (10 grams) B.P. 40- 75° at 50 mm.

II. Fraction (53 grams) B.P. 75- 85° at 50 mm.

III. Fraction (27 grams) B.P. 85-100° at 50 mm.

The low boiling fraction was unreacted acid halide and aldehyde and the high boiling other condensation products. Fraction II was composed largely of the halogenated ester and after several rectifications, yielded a product B.P. 78-81° at 50 mm., which was α chloro iso-butyl acetate. The yield was 59%. The halogenated ester was a heavy, colorless liquid, which turned dark on standing, decomposing readily.

Subst., 0.3254; AgCl, 0.3070.

Calc. for $C_6H_{11}O_2Cl$: Cl, 23.6. Found, 23.5.

Isobutyl Aldehyde and Propionyl Chloride=

$$CH_3CH_2CO\text{-}O\text{-}CHClCH\begin{matrix} CH_3 \\ CH_3 \end{matrix}$$, α chloro iso-butyl propionate.

64 grams of propionyl chloride and 50 grams of isobutyl aldehyde were weighed out in a round bottom flask. A violent reaction occurred upon mixing the two chemicals which was completed by

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heating on the water bath at 90° for 1 hour. The dark liquid was distilled under diminished pressure, the product boiling at 50-120° at 18 mm. The distillate was then refractionated several times under diminished pressure and separated into the following portions.

I. Fraction (10 grams) B.P. 50-65°, at 18 mm.

II. Fraction (41 grams) B.P. 65-75°, at 18 mm.

III. Fraction (15 grams) B.P. 75-120°, at 18 mm.

The middle fraction was composed largely of the halogenated ester and after several redistillations in vacuum yielded a product boiling constant at 67-70° at 18 mm. and was α chloro isobutyl propionate. The yield was 60%. The heavy, colorless liquid possessed a sharp odor, and decomposed on standing.

Subst., 0.1740; AgCl, 0.1535

Calc. for $C_7H_{13}O_2Cl$: Cl, 21.55. Found, 21.8.

Isobutyl Aldehyde and Butyryl Chloride= $CH_3CH_2CH_2C(=O)-O-CHClCH(CH_3)_2$

α Chloro Isobutyl Butyrate

74 grams of butyryl chloride and 50 grams of isobutyl aldehyde were placed in a round bottom flask. There was a vigorous reaction immediately, which was completed by heating on the water bath at 90° for 1 hour. After this time, the reaction mixture, which had turned dark, was distilled under diminished pressure, the entire product boiling at 40-120° at 10 mm. The distillate was then separated into three portions by repeated fractionations in vacuum as follows:

I. Fraction (25 grams) B.P. 40- 70° at 10 mm.

II. Fraction (50 grams) B.P. 70- 80° at 10 mm.

III. Fraction (12 grams) B.P. 80-120° at 10 mm.

Fraction II made up the largest portion of the distillate

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and was composed chiefly of the halogenated ester. After several distillations, a product was obtained boiling constant at 74-76° at 10 mm. and was α chloro isobutyl butyrate. The yield of the halogen ester was 56%. The condensation product was a heavy colorless liquid, which decomposed somewhat on standing.

Subst.; 0.3481. AgCl, 0.3100.

Calc. for $C_8H_{15}O_2Cl$: Cl, 19.9. Found, 19.8.

Isobutyl Aldehyde and Valeryl Chloride=

$CH_3CH_2CH_2CH_2COO\text{-}CHClCH\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$ α Chloro Isobutyl Valerate

65 grams of valeryl chloride and 36 grams of isobutyl aldehyde were weighed out in a round bottom flask. A vigorous reaction ensued immediately and the liquid boiled for some time from its own heat of reaction. After heating on the water bath at 90° for 1 hour, the dark colored reaction mixture was distilled under diminished pressure, the entire product boiling at 50-140°, at 6 mm. The distillate was then separated into three portions by repeated fractional distillations in vacuum, as follows:

I. Fraction (10 grams) B.P. 50- 78° at 6 mm.

II. Fraction (45 grams) B.P. 78- 86° at 6 mm.

III. Fraction (15 grams) B.P. 86-140° at 6 mm.

Fraction II consisted largely of the halogenated ester and after several refractionations yielded a product boiling constant at 80-83° at 6 mm. and which was α chloro isobutyl valerate. The yield of the halogen ester was 64%. The addition product was a heavy colorless liquid, when freshly distilled, but turned dark on standing.

Subst. 0.1984; AgCl, 0.1491.

Calc. for $C_9H_{17}O_2Cl$: Cl, 18.45. Found, 18.6.

Isobutyl Aldehyde and Acetyl Bromide= $CH_3CO{-}O{-}CHBrCH\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}$,

α Bromo iso-butyl acetate.

122 grams of acetyl bromide and 72 grams of isobutyl aldehyde were weighed out in a round bottom flask. The reaction took place vigorously and characteristic of all the aliphatic acid bromides condensed with aliphatic aldehydes. The reaction was completed by heating on the water bath at 90° for one hour, after which the liquid was distilled, under diminished pressure, the product boiling from 48-100° at 30 mm. The distillate was then fractionally distilled in vacuum as follows:

I. Fraction (10 grams) B.P. 48- 70° at 30 mm.

II. Fraction (50 grams) B.P. 70- 78° at 30 mm.

III. Fraction (15 grams) B.P. 78-100° at 30 mm.

Fraction II consisted mainly of the halogenated ester. After several fractionations, a product boiling constant at 73-75° at 30 mm. was obtained which proved to be α bromo isobutyl acetate. The yield was 66%. The condensation product was a heavy liquid possessing a sharp odor and was colorless when freshly distilled. It was more easily decomposed than the corresponding addition product with acetyl chloride.

Subst., 0.2030; AgBr, 0.1946.

Calc. for $C_6H_{11}O_2Br$: Br, 41.0. Found, 40.8.

4. Addition Products with Iso-Valeryl Aldehyde.

Iso-Valeryl Aldehyde and Acetyl Chloride= $CH_3CO{-}O{-}CHClCH_2CH\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}$,

α Chloro Iso-Valeryl Acetate.

The iso-valeryl aldehyde was prepared from iso-amyl alcohol in a manner exactly analogous to iso-butyl aldehyde from isobutyl alcohol, as cited above. The product boiling at 90-93° at

750 mm. was used. 39 grams of acetyl chloride and 43 grams of the aldehyde were placed in a round bottom flask and heated on the water bath at 90° for 1 hour. The liquid, which had turned dark colored during the reaction was distilled under diminished pressure. The mixture boiled at 30-100° at 60 mm. The distillate was fractionated in vacuum three times and separated into the following portions:

I. Fraction (10 grams) B.P. 30 -85° at 60 mm.

II. Fraction (40 grams) B.P. 85 -95° at 60 mm.

III. Fraction (8 grams) B.P. 95-100° at 60 mm.

The three fractions were further distilled until a constant boiling product, 89-93° at 60 mm., was obtained. This portion was α chloro iso-valeryl acetate. The yield of halogenated ester was 69%. The product was a colorless, heavy liquid, with a pleasant odor and was quite stable.

Subst., 0.2300; AgCl, 0.1980.

Calc., for $C_7H_{13}O_2Cl$: Cl, 21.6. Found, 21.3.

Iso-Valeryl Aldehyde and Acetyl Bromide=$CH_3CO-O-CHBrCH_2CH\begin{matrix} \diagup CH_3 \\ \diagdown CH_3 \end{matrix}$,

α Bromo Iso-Valeryl Acetate.

62 grams of the acid bromide and 43 grams of the aldehyde were weighed out in a round bottom flask and heated on the water bath at 90° for 1 hour. The two chemicals reacted very violently on mixing and turned dark during the reaction. The product was distilled under diminished pressure, the entire liquid boiling at 30-105° at 25 mm. The distillate was then fractionated several times in vacuum and separated as follows:

I. Fraction (30 grams) B.P. 30- 80° at 25 mm.

II. Fraction (62 grams) B.P. 80- 90° at 25 mm.

III. Fraction (8 grams) B.P. 90-105° at 25 mm.

Repeated distillations of the several fractions finally gave a product boiling constant at 85-88° at 25 mm. It was α bromo iso-valeryl acetate. The heavy, colorless liquid decomposed readily on standing. The yield was 63%.

Subst., 0.3400; AgBr, 0.2134.

Calc. for $C_7H_{13}O_2Br$: Br, 38.3. Found, Br, 37.9.

5. Addition Products with Heptaldehyde.

Heptaldehyde and Acetyl Chloride=CH_3CO-O-$CHCl(CH_2)_5CH_3$, α chloro heptyl acetate.

The heptaldehyde used was a commercial product, redistilled twice and collecting the fraction boiling at 154-156° at 750 mm. as pure enanthol. 85 grams of the aldehyde and 58 grams of acetyl chloride were placed in a round bottom flask. A reaction commenced immediately on mixing the two liquids which was completed by heating on the water bath at 90° for 1 hour. The dark liquid was then distilled under diminished pressure, the product boiling from 45-145° at 15 mm. The distillate was separated into three portions by fractional distillation in vacuum.

I. Fraction (10 grams) B.P. 45-100° at 15 mm.

II. Fraction (70 grams) B.P.100-110° at 15 mm.

III. Fraction (20 grams) B.P.110-145° at 15 mm.

After several fractional distillations, a product boiling constant at 104-105° at 15 mm. was obtained. It was α chloro heptyl acetate. The yield of the ester was 60%. The addition product was a heavy, stable oil, colorless and possessing a pleasant odor.

Subst., 0.2680. AgCl, 0.2026.

Calc. for $C_9H_{17}O_2Cl$: Cl, 18.45. Found Cl, 18.73.

Heptaldehyde and Butyryl Chloride=$CH_3CH_2CH_2CO$-O-$CHCl(CH_2)_5CH_3$ α chloro heptyl butyrate

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

85 grams of heptaldehyde and 79 grams of butyryl chloride were placed in a round bottom flask and heated on the water bath at 90° for an hour. The dark liquid was then distilled under diminished pressure, the entire product boiling at 40-160° at 15 mm. The distillate was redistilled in vacuum and the following fractions collected.

I. Fraction (35 grams) B.P. 40-118° at 15 mm.

II. Fraction (90 grams) B.P.118-126° at 15 mm.

III. Fraction (25 grams) B.P.126-160° at 15 mm.

After repeated fractional distillations, a product was obtained, boiling constant at 120-122° at 15 mm., which was α chloro heptyl butyrate. The yield was 60%. The halogenated ester was a heavy, colorless oil of pleasant odor and unstable.

Subst., 0.1660; AgCl, 0.1100.

Calc. for $C_{11}H_{21}O_2Cl$: Cl, 16.1. Found, 16.38.

Heptaldehyde and Acetyl Bromide, $CH_3CO-O-CHBr(CH_2)_5CH_3$, α bromo heptyl acetate.

57 grams of the aldehyde and 61 grams of the acid bromide were mixed together in a round bottom flask and heated on the water bath at 90° for 1 hour. The reaction proceeded violently at first, which is characteristic of the acid bromides. The reaction mixture turned dark during the process. The liquid was then distilled under diminished pressure, the product boiling at 60-140° at 15 mm. The distillate was again fractionated several times in vacuum as follows:

I. Fraction (18 grams) B.P. 60-110° 15 mm.

II. Fraction (60 grams) B.P.110-120° 15 mm.

III. Fraction (30 grams) B.P.130-140° 15 mm.

After several fractional distillations, a product was obtained boil-

ing constant at 113-116° at 15 mm. which was the halogenated ester. The yield was 65%. α bromo heptyl acetate was a heavy colorless oil when pure, decomposing readily on standing.

Subst. 0.3813. AgBr, 0.3220

Calc. for $C_9H_{17}O_2Br$: Br, 33.7. Found, 33.55.

B. Reactions of Aromatic Acid Halides and Aliphatic Aldehydes.

1. Addition Products with Paraformaldehyde

Paraformaldehyde and Benzoyl Chloride=$C_6H_5CO\text{-}O\text{-}CH_2Cl$, chlormethyl benzoate.

The benzoyl chloride used was prepared from fused benzoic acid and phosphorus pentachloride. The product boiling at 88° at 15 mm. was employed. The paraformaldehyde was carefully dried. 30 grams of the aldehyde and 140 grams of acid chloride were placed in a round bottom flask and heated on the water bath at 90° until the paraformaldehyde had entirely disappeared. After the reaction, no odor of benzoyl chloride was perceptible and the liquid had turned slightly brown during the process. The reaction mixture was then distilled under diminished pressure. 35 grams of a solid remained in the distilling flask which after recrystallization from alcohol melted at 100° and was the dibenzoate of methylene, $(C_6H_5COO)_2CH_2$. The main portion of the distillate, after several fractionations in vacuum, boiled at 114-115° at 8 mm. and was chloro methyl benzoate. Descude[11] reports the boiling point of the halogenated ester as 116° at 10 mm. The yield was 60%. Chloro methyl benzoate is a heavy, colorless, stable oil with a penetrating odor.

Paraformaldehyde and p-Chlor Benzoyl Chloride

The p-chlor benzoyl chloride was prepared from p-chlor benzoic acid by the action of phosphorous pentachloride. The acid

chloride boiled at 123-5° at 26 mm. 30 grams of p-chlor benzoyl chloride and 5.1 grams of dry paraformaldehyde were heated on the water bath at 95° until the paraformaldehyde had disappeared (6 hrs.) The flask was then removed from the water bath and allowed to cool; a solid separated out, only slightly soluble in ether. The reaction mixture was then treated with anhydrous ether and the solid filtered off by suction. The solid was methylene di-p-chloro benzoate. There was 6 grams. The ether soluble product was transferred to a fractionating flask and the ether distilled off under atmospheric pressure and finally the residual oil under diminished pressure. After several fractionations, 5 grams of unreacted acid chloride, B.P. 120° at 20 mm., and 16 grams of chlor methyl p-chlor benzoate, B.P. 163-5° at 30 mm., was obtained. The yield was 50%. The halogenated ester was a heavy, colorless liquid, stable and possessing a sharp odor.

Subst. 0.2340; AgCl, 0.3260.

Calc. for $C_8H_6O_2Cl_2$: Cl, 34.64. Found, 34.5

Paraformaldehyde and Benzoyl Bromide= $C_6H_5C{\overset{O}{\lessdot}}-OCH_2Br$, Bromomethyl-benzoate.

The benzoyl bromide was prepared from fused benzoic acid and oxalyl bromide[20]. The product used boiled at 218-220° at 739 mm. 50 grams of the acid bromide and 8.3 grams of dry paraformaldehyde were heated in a round bottom flask on the water bath at 90° until the paraformaldehyde had disappeared (3 hours). The reaction mixture was then fractionated under diminished pressure. 30 grams of brom methyl benzoate was obtained, B.P. 135-137° at 18 mm. The yield was 50%. 12 grams low boiling product, B.P. 100-135° at 18 mm., was recovered, largely unreacted benzoyl bromide. 14 grams of the dibenzoate of methylene, M.P. 100°, crystallized from alcohol, was also obtained. The bromoester was a very heavy, colorless liq-

uid, with an odor similar to that of the corresponding chloro-ester.

Subst. 0.1920; AgBr, 0.1680.

Calc. for $C_8H_7O_2Br$: Br, 37.2. Found, 37.25.

2. Addition Products with Paraldehyde.

Paraldehyde and Benzoyl Chloride=$C_6H_5COO-CHClCH_3$, α Chloro Ethyl Benzoate.

176 grams of benzoyl chloride and 75 grams of paraldehyde were weighed out in a round bottom flask, and heated on the water bath at 90° for an hour. At the end of this time, the dark reaction mixture was allowed to cool; a solid crystallized out which was filtered off by suction and which proved to be benzoic acid, M.P. 120°. 10 grams of the solid was recovered. The filtrate from the benzoic acid was then fractionated several times in vacuum until a product boiling constant at 130° at 8 mm. was obtained which was the halogenated ester. There was 148 grams of the product, making the yield 60%. 50 grams of distillate, B.P. 80-118° at 8 mm., composed largely of unreacted benzoyl chloride, was also obtained together with 15 grams of a high boiling solid, the dibenzoate, but which was not identified. Descude[11] mentions that a condensation product between benzoyl chloride and paraldehyde could not be isolated by him. α Chloroethyl benzoate was a heavy, colorless liquid, with a somewhat pleasant ester odor and was stable.

Subst. 0.1750; AgCl, 0.1370.

Calc. for $C_9H_9O_2Cl$: Cl, 19.25. Found, 19.3.

3. Addition Products with n-Butyl Aldehyde.

n-Butyl Aldehyde and Benzoyl Chloride= $C_6H_5CO-OCHClCH_2CH_2CH_3$, α chloro n-butyl benzoate.

The n-butyl aldehyde was prepared from n-butyl alcohol by oxidation with sodium dichromate as mentioned above. 70 grams of

benzoyl chloride was weighed out in a round bottom flask. 36 grams of n-butyl aldehyde was then slowly added to the acid chloride from a dropping funnel, and the mixture refluxed gently with a free flame for 1/2 to 3/4 hours. It was thought that this method of adding the aldehyde would reduce to a minimum aldol condensations, with the subsequent formation of water and thus reduce the amount of benzoic acid formed by hydrolysis. Since it was found that the condensation products between benzoyl chloride and aliphatic aldehyde were comparatively stable to water and dilute sodium carbonate, the benzoic acid was removed from ether solution by this method; 25 grams was recovered. The ether layer was separated, dried with $CaCl_2$ and distilled-- the ether under ordinary pressure and the residual oil in vacuum. After repeated fractionations, the following products were obtained:

I. Fraction (15 grams) B.P. 85 -91° at 18 mm.

II. Fraction (40 grams) B.P.135-138° at 18 mm.

III. Fraction (20 grams) B.P.150-200° at 18 mm.

The low boiling fraction was largely unreacted benzoyl chloride. The middle fraction composed 45% of the products and was α chloro-n-butyl benzoate. The high boiling fraction was made up of high boiling condensation products. The halogenated ester was a heavy liquid with an ester odor which gradually turned brown on standing.

Subst. 0.2563; AgCl, 0.1700

Calc. for $C_{11}H_{13}O_2Cl$: Cl, 16.7. Found, 16.4%.

4. Addition Products with Iso-valeryl Aldehyde.

Iso-valeryl Aldehyde and Benzoyl Chloride=

$C_6H_5CO-O-CHCl-CH_2-CH\begin{matrix} \diagup CH_3 \\ \diagdown CH_3 \end{matrix}$ α chloro-iso-valeryl benzoate

40 grams of benzoyl chloride was placed in a round bottom

flask and attached to a condenser. 43 grams of isovaleryl aldehyde, prepared by the oxidation of iso-amyl alcohol, was slowly added from a dropping funnel and the two liquids refluxed gently for 3/4 hours. The reaction mixture was allowed to cool and treated with ether and 10% Na_2CO_3 to remove the benzoic acid formed. 20 grams was recovered. The ether layer was separated, dried with $CaCl_2$ and distilled. After several fractional distillation in vacuum, 45 grams of a product boiling at 145-147° at 18 mm. was obtained. It was α chloro-isovaleryl benzoate. The compound was a heavy oil, with a somewhat pleasant odor, and stable. 15 grams of a low boiling, 80-130° at 18 mm., and 20 grams of a high boiling product, 150-200° at 18 mm., was likewise obtained in the run. The yield of the halogen ester was 50%.

Subst. 0.2114; AgCl, 0.1325.

Calc. for $C_{12}H_{15}O_2Cl$: Cl, 15.65. Found, 15.5.

5. Addition Products with Heptaldehyde.

Heptaldehyde and Benzoyl Chloride= C_6H_5CO-O-$CHCl(CH_2)_5CH_3$,

α Chloro Heptyl Benzoate.

70 grams of a benzoyl chloride and 57 grams of heptaldehyde were allowed to react, and the products worked up in a manner similar to the reaction products between benzoyl chloride and n-butyl, and iso-valeryl aldehydes. In this experiment, 45 grams of the halogen ester was obtained, which after several redistillations in vacuum boiled at 180-183° at 18 mm. The yield was 40%. Lees[10] reports the preparation of the vinyl ester C_6H_5CO-O-$CH=CH(CH_2)_5CH_3$, B.P. 195° at 50 mm., by the action of benzoyl chloride on heptaldehyde and refluxing the reaction mixture from 4 - 6 hours, intimating that the halogen ester may form as an intermediate, which by subse-

quent loss of halogen acid forms the unsaturated ester. It is noticeable that refluxing for only a short time produced the halogen ester in fair yield. The fact that prolonged heating of the halogen ester at 25° was followed by loss of halogen acid was proved by making a run, using the exact methods employed by Lees. In this experiment, the halogen ester was entirely decomposed and 50 grams of the unsaturated ester, B.P. 135-137° at 45 mm., was obtained. Refluxing the reaction mixture for only a short time yielded 45 grams of α chloro heptyl benzoate, while only 13 grams of the unsaturated ester, B.P. 167-70° at 18 mm. formed. 10 grams of unchanged aldehyde, B.P. 65-70° at 18 mm., and 15 grams of unreacted benzoyl chloride, B.P. 88-90° at 18 mm., was also recovered. It is significant to note that the corresponding unsaturated esters from benzoyl chloride and n-butyl and iso-valeryl aldehyde could not be prepared. This may possibly be explained by the fact that the temperature attained at the respective boiling points of the two halogen esters was not sufficiently high to split out halogen acid. α chlor heptyl benzoate was a heavy, colorless oil which turned slightly brown on standing.

Subst. 0.2382; AgCl, 0.1365.

Calc. for $C_{14}H_{19}O_2Cl$: Cl, 13.95. Found, 13.68.

Reactions between Aromatic Aldehydes and Aliphatic Acid Chlorides.

Benzaldehyde and Acetyl Chloride.

For two months, it was endeavored to isolate the condensation product between benzaldehyde and acetyl chloride, namely phenyl chloro methyl acetate. The condensation product either did not form under the conditions employed, or if the compound did form it could not be distilled under diminished pressure without decomposition.

Many experiments were tried, under different conditions, to isolate the condensation product but met with no success. Allowing equimolecular quantities of the aldehyde and acid chloride, with and without $ZnCl_2$, to stand at room temperature for several days was not successful. There seemed to be a reaction on mixing the two chemicals accompanied by an evolution of heat. But upon attempting to distill the reaction mixture after the unchanged aldehyde and acetyl chloride came over, there was always left a tarry, high boiling resin which invariably decomposed, no matter how low a vacuum was obtained, nor could the resin be crystallized out by a freezing mixture. The distillation was rendered difficult in that the volatile acetyl chloride could not be condensed properly in a vacuum distillation and thus prevented a low pressure. However, this was remedied by using a trap, which was surrounded by carbon dioxide snow. At the temperature of CO_2-snow, the acetyl chloride was condensed and as low a vacuum as 3 mm. was obtained with a Cenco oil pump. However, even at this low vacuum the resin decomposed. As only small amounts of the resin were obtained at room temperature, it was endeavored to increase the amount formed in a run and if possible to crystallize it out. Therefore, molecular quantities of the aldehyde and acetyl chloride were heated on the water bath for varying lengths of time (1 - 48 hours) and even refluxing the reaction mixture with a free flame was resorted to without success. The nature of the resin could not be determined.

C. Reactions of the Addition Compounds.

1. With Ammonia and Amines.

Chloromethyl Acetate with Ammonia and Aliphatic Amines

Passing dry ammonia gas into an anhydrous ether solution

[illegible]

of chloromethyl acetate, produced as the chief products of the reaction, acetamide, ammonium chloride and formaldehyde.

Under the same conditions, primary and secondary aliphatic amines, mono-methyl and di-ethyl amine, gave the substituted acid amides, the amine hydrochloride and formaldehyde.

Choro methyl acetate and Aniline.

Treating an absolute ether solution of chloro methyl acetate with 2 mols of aniline, there was produced chiefly phenyl acetamide or acetanalid, aniline hydrochloride and formaldehyde. Thus, from 20 grams of chloromethyl acetate, treated with 25 grams of aniline in anhydrous ether was obtained 30 grams of acetanilid, M.P. 114-115°. 15 grams of a yellow solid separated from the ether. On treating the solid with water, a portion was soluble and on making the solution alkaline, an oil separated which was identified as aniline. The water insoluble portion was anhydro-formaldehyde aniline, described by Goldschmidt[30] and produced by the action of formaldehyde (liberated from chloromethyl acetate) upon the excess of aniline. It melted at 140-141°, the same as given in the literature. Boiling with aqueous alkali decomposed the compound into aniline and formaldehyde. The aniline was identified by the phenyl isocyanide given with chloroform.

On treating 20 grams of chloromethyl acetate with 37.5 g. of diethyl aniline, there was apparently no reaction in the cold.

Chloromethyl Benzoate and Ammonia.

The action of ammonia upon $C_6H_5COOCH_2Cl$, chloromethyl benzoate, was illustrated by the following experiment. 20 grams of chloromethyl benzoate was dissolved in 100 cc. of anhydrous ether

and dry ammonia gas was passed into the solution at room temperature until no further precipitate was produced. The solid was filtered off by suction and treated with hot benzene. On cooling 5 grams of benzamide, M.P. 128°, separated. The portion of the solid remaining after extraction with hot benzene was identified as ammonium chloride. It dissolved in water, gave a precipitate of silver chloride and liberated ammonia on treating with alkali. On evaporating the ether from the ether soluble portion 8 grams of benzamide, M.P. 128°, was also obtained.

Chloromethyl Benzoate and Diethylamine.

15 grams of chloromethyl benzoate was dissolved in 100 cc. of dry ether and 12.8 grams of diethylamine added. A white solid separated at once. The reaction mixture was allowed to stand for 24 hours and then the solid was filtered off. It proved to be diethylamine hydrochloride, M.P. 200-205°. The solid was soluble in water and on treating with alkali, the odor of diethylamine was observed. There was 5 grams of the hydrochloride. On evaporating the ether from the ether soluble portion, 8 grams of an oil was obtained, b.p. 173-175° at 35 mm., which corresponded in properties to diethyl benzamide.

Chloromethyl Benzoate and Aniline.

15 grams of chloromethyl benzoate, dissolved in 75 cc. of dry ether, was treated with 16.4 grams of aniline and allowed to stand for 24 hours. A yellow precipitate separated immediately. The solid was filtered off by suction. It was a mixture of aniline hydrochloride and anhydro formaldehyde aniline. The aniline hydrochloride was removed by extraction with water. The anhydroformaldehyde aniline melted at 140-141°; there was 6 grams. The ether was

distilled off the ether soluble product and 10 grams of a white solid remained which after recrystallizing from alcohol melted at 159-160°. It was benzanalid.

Chloromethyl Benzoate and Diethyl Aniline.

On allowing 10 grams of chloromethyl benzoate and 8.7 g. of diethyl aniline to stand at room temperature for 24 hours, there was no heat involved. There was apparently no reaction and the original substances were obtained unchanged.

2. With Water.

5 cc. of chloromethyl acetate and chloroethyl acetate respectively were treated with 5 cc. of water and allowed to stand. The liquids were immiscible at the beginning of the experiment but after 24 hours the halogen esters had gone completely into solution, decomposing into acetic acid, hydrochloric acid and the corresponding aldehydes.

In a similar manner, 5 cc. of chloromethyl benzoate and chloroethyl benzoate were treated with 5 cc. of water and allowed to stand in stoppered test tubes. These esters in contrast to the aliphatic esters were exceedingly stable and showed no signs of decomposition after two weeks. Benzoyl chloride, on the other hand, had largely decomposed to benzoic acid in 24 hours when treated in a similar fashion.

3. With Solid Potassium Hydroxide.

Chloromethyl Acetate and Potassium Hydroxide.

When 25 grams of chloromethyl acetate was heated on the water bath at 30° with an equimolecular quantity of solid KOH, it decomposed, practically quantitatively, into potassium acetate,

potassium chloride and formaldehyde.

α Chloroheptyl Acetate and KOH.

The action of solid KOH on α chloroheptyl acetate was next studied. 25 grams of the halogen ester was treated with 1 mol of solid KOH and heated on the water bath. The primary object of the experiment was to split out hydrochloric acid from the halogen ester to form the unsaturated vinyl derivative. However, instead most of the halogen ester was decomposed to potassium acetate, potassium chloride and heptaldehyde.

Chloromethyl Benzoate, α Chloro Iso-valeryl Benzoate, and α Chloroheptyl Benzoate with KOH.

Similarly, chloromethyl benzoate, α chloro iso-valeryl benzoate and α chloroheptyl benzoate were treated with solid KOH, and in no case was the vinyl ester or vinyl derivative obtained, but instead potassium benzoate, potassium chloride and the corresponding aldehyde.

4. With Pyridine.

Chloromethyl Acetate and Pyridine.

When 20 grams of chloromethyl acetate was treated with 14.5 grams (1 mol) of pyridine, there was heat evolved. The two liquids were miscible but on standing for a short time, a heavy dark colored oil separated which could not be purified for analysis, either by crystallization or distillation in vacuo. The liquid decomposed on heating. Qualitative analysis showed the presence of nitrogen and halogen. Therefore, it was inferred that the oil was probably the pyridine addition compound of chloromethyl acetate.

α Chloroheptyl Acetate and Pyridine.

50 grams of α chloroheptyl acetate was treated with 41 grams (3 mols) of pyridine and allowed to stand for 3 days. The object of the experiment was either to prepare the pyridine addition compound of the halogenated ester or to pull out halogen acid from chloroheptyl acetate to form the vinyl derivative. At the end of 3 days, the liquid, which showed no signs of a reaction either by the formation of a solid or an oil, was treated with ether and HCl to remove the excess of pyridine. The ether layer was separated, dried with $CaCl_2$ and distilled. Practically all of the halogen ester, B.P. 105-108° at 20 mm., was recovered. A similar experiment was run with α chloroheptyl acetate and pyridine, heating the two on a water bath for 24 hours with the same result. The halogenated ester was recovered unchanged and apparently was stable and did not lose halogen acid easily, nor did this particular ester have the property of forming a pyridine addition compound.

The next experiment was run, following the directions of Claisen and Haase[38] for the determination of the enol form of aceto-acetic ester in which was isolated o-acetyl aceto acetic ester. 57 grams of heptaldehyde and 79 grams of pyridine were placed in a round bottom flask and attached to a water condenser. 58 grams of acetyl chloride was added slowly from a dropping funnel. Each drop of acetyl chloride reacted vigorously with the formation of a solid. The reaction mass was kept cool with ice until all of the acetyl chloride was added. The semi-solid mass was allowed to stand for 24 hours and then treated with water and ether. The water destroyed the excess of acetyl chloride, the ether layer was then separated and treated with HCl to remove the excess of pyridine. The ether layer was again separated, washed with H_2O twice and dried with

$CaCl_2$. The solvent was distilled off and finally the residual oil under diminished pressure. Most of the aldehyde (40 grams), B.P. 65° at 18 mm., was recovered, and no unsaturated ester. The acetyl chloride reacted with the pyridine to form a salt and was removed by the water. A similar experiment was run, heating the reaction mixture on the water bath for 24 hours. The unsaturated ester was not formed in this case.

Semmler[29] reports the preparation of the unsaturated ester from heptaldehyde, acetic anhydride, and sodium acetate. This he calls enol n-heptonal acetate, $CH_3COOCH{=}CH(CH_2)_4CH_3$, B.P. 76-9° at 10 mm.

Chloromethyl Benzoate and Pyridine.

15 grams of chloromethyl benzoate and 10 grams of pyridine were weighed out in a small Erlenmeyer flask and allowed to stand. There was no heat evolved on mixing the two chemicals and in a short time crystals began to form, the mixture solidifying entirely after 6 hours. The excess of pyridine was filtered off the crystals by suction. The deliquescent solid was purified by twice dissolving in absolute alcohol and precipitating with absolute ether. The pure white crystals melted at 177-178°. It was the pyridine addition compound of chloromethyl benzoate.

Subst., 0.4796, required 18.75 cc. $AgNO_3$. N.F.0.1033

Calc. for $C_{13}H_{12}O_2NCl$: Cl, 14.23. Found, 14.20.

α Chloroethyl Benzoate and Pyridine.

α Chloroethyl benzoate treated similarly with pyridine formed a semi-solid viscous mass, dark colored and which could not be purified. On treating the reaction mixture with HCl to remove

the excess of pyridine and ether, separating the ether layer, drying with $CaCl_2$ and distilling no vinyl benzoate was recovered. The latter compound had either not formed, or if halogen acid had split out the vinyl benzoate formed decomposed during the reaction.

α Chloro Iso-valeryl Benzoate and α Chlorheptyl Benzoate with Pyridine.

In the same way, treating α chloro iso-valeryl and α chloro heptyl benzoate with pyridine, neither the pyridine addition compound nor pyridine hydrochloride and the unsaturated ester was formed but on working up the reaction mixtures most of the halogen ester was recovered unchanged.

Again, treating 57 grams of heptaldehyde and 79 grams of pyridine, with 70 grams of benzoyl chloride according to the method of Claisen and Haase cited above was not successful in isolating the α, β unsaturated heptylene benzoate. This compound has been prepared by Lees[10] by continued refluxing of benzoyl chloride and n-heptaldehyde at a high temperature.

5. With Quinoline.

Chloromethyl Acetate and Quinoline.

20 grams of chloromethyl acetate and 14.5 grams of quinoline were weighed out in a small Erlenmeyer flask, and allowed to stand. After 24 hours the liquid had solidified. The solid was purified by dissolving in absolute alcohol and precipitating with absolute ether. Two precipitations gave a slightly colored solid melting with decomposition at 314-316°. It was the quinoline addition compound of chloromethyl acetate.

Subst., 0.[illegible]20; required 31.48 cc. $AgNO_3$, N.F.0.1022

Calc. for $C_{12}H_{12}O_2NCl$: Cl, 14.95. Found, 15.20.

Chloromethyl Benzoate and Quinoline.

Chlormethyl benzoate and quinoline reacted to form a red, viscous oil, presumably the quinoline addition compound, but which could not be made to solidify for purification.

V. SUMMARY

1. The reactions between aliphatic acid halides and aliphatic aldehydes, and between aliphatic aldehydes and aromatic acid chlorides to give halogenated esters are general, just as is the case with aromatic acid halides previously prepared.

2. Addition compounds between formaldehyde , acetaldehyde, n-butyl, iso-butyl, iso-valeryl, and heptaldehydes, with simple and substituted aliphatic acid halides have been prepared.

3. The halogenated ester addition products between formaldehyde, acetaldehyde, n-butyl, iso-valeryl and heptaldehydes, with aromatic acid chlorides have been prepared.

4. The addition compounds between aromatic aldehydes and aliphatic acid halides, such as phenyl chloro methyl acetate could not be prepared.

5. The structure of the aliphatic-aliphatic and aromatic-aliphatic addition compounds has been indicated, as outlined by previous work and certain reactions carried out in the present research.

6. The formation of the various types of halogenated esters involves widely different methods of preparation. In some cases the compounds form at room temperature, while in others a high temperature is necessary for addition to take place.

7. In general it has been found that acid bromides react with aldehydes with greater rapidity and with more violence than acid chlorides.

8. The stability of the various types of halogenated esters varies as follows: the aromatic acid chloride-aliphatic aldehyde addition compounds are the most stable, the aliphatic acid halide-formaldehyde and acetaldehyde compounds next and the higher

aliphatic aldehyde-aliphatic acid halide halogenated esters the least stable.

9. The different types of halogenated esters form with greater ease and higher yields are obtained in the aliphatic-aliphatic series than in the aromatic-aliphatic.

10. The action of ammonia, certain amines, water, potassium hydroxide, pyridine and quinoline, on chloro methyl acetate and benzoate has been studied. The reactions of the halogenated esters in some cases are such as might be expected from a mere mixture of the aldehyde and acid halide used, while in others the reactions are characteristic of the addition compounds.

VI. BIBLIOGRAPHY

1. Adams and Volwiler. J.A.C.S. 40, 1732 (1918).
2. French, H.E. Doctor's Thesis, University of Illinois, 1920.
3. Wurtz, Ann., 102, 94 (1857).
4. Simpson, Ann. 109, 156 (1859).
5. Franchimont, Recueil. I, 243 (1882).
6. Schiff, Ber., 9, 304 (1876).
7. Geuther, Ann., 106, 250 (1858).
8. Ruoencamp, Ann., 225, 274 (1884).
9. Henry, Bull. acad. roy. belg., 1900, p. 48.
10. Lees, J. Chem. Soc., 83, 145 (1903).
11. Descude, Ann. chim., (7) 29, 488 (1903).
12. Paal, Ber., 15, 1818 (1882); 17, 911 (1884).
13. Wöhler and Liebig, Ann., 3, 266 (1832).
14. Claisen, Ber. 14, 2473 (1881).
15. Laurent and Gerhardt Cr. (1850), 123.
16. Schiff, Ann., 154, 347 (1870).
17. Staudinger and Anthes, Ber. 46, 1425 (1913).
18. Staudinger, Ber. 42, 3966 (1909).
19. Wegscheider and Spath, Monatsh., 30, 863 (1909).
20. Adams and Ulich, J.A.C.S. 42, 599, 1920.
21. Vanino, II, 164.
22. Henry, Cr., 133, 97 (1901).
23. Hell, Ber. 14, 891 (1881).
24. Volhard, Ann. 242, 141 (1887).
25. Zelinsky, Ber. 20, 2026 (1887).
26. Noyes, J.A.C.S. 39, 2718 (1917).
27. Vanino, II, 51.
28. Claisen & Haase, Ber. 33, 1243 (1900).
29. Semmler, Ber. 42, 1161 (1909).
30. Goldschmidt, C. i, 227 (1905).

VII. BIOGRAPHY

The writer of this thesis was born in Creston, Iowa, January 2, 1892. He entered Grinnell College (Iowa) in 1910 and received the B.S. Degree in 1914. From 1914 - 1915, he was instructor of Science and Mathematics in the Albia (Iowa) High School, and the following year, 1915 - 1916, he occupied the same position at Windom College, Montevideo, Minnesota. In the fall of 1916, he entered the University of Illinois as a graduate student with the rank of Graduate Assistant in Chemistry. From 1917-1918 he was Assistant in Chemistry at the same Institution, receiving the M.S. Degree in 1918. From 1918 - 1919, he was a DuPont Fellow in Chemistry at the University of Illinois, and the following year, 1919 - 1920, he was Fellow in Chemistry at the same University. His publications consist of one paper: "The Use of Oxalyl Chloride and Bromide for Producing Acid Chlorides, Acid Bromides, or Acid Anhydrides" by Dr. Roger Adams and L. H. Ulich, J. Am. Chem. Soc., 42, 599 (1920).